EFFECT OF ROTATION SPEED AND TEMPERATURE TO WAX DEPOSITION FOR MALAYSIAN CRUDE OIL

FAZERAH BINTI MOEN

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UNIVERSITI MALAYSIA PAHANG

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ABSTRACT

Wax depositions have been a major problem in the oil and gas field. It generates additional pressure drop and causes fouling which ultimately increase the operating cost during production, transportation, and handling of waxy crude oil. The problem are initiated due to the decrease of crude oil temperature during the transportation process which eventually caused the solidified of the crude oil to form wax. The deposited wax is normally removed by pigging process. The wax deposition of the crude oil in the pipeline makes the flow area smaller and smaller with time, which then influences the transportation capacity and the operation safety of the pipeline. There are many factors that influence the wax deposition: the crude components, the carbon atom distribution of the paraffin, the oil temperature, the temperature difference between the oil and the pipe wall, the deposition duration, the flow rate, and so on. In this research the effect of rotation speed was investigated toward the wax deposition. In addition, the temperature effect to the wax solubility is also been studied. The experimental work were conducted using cold finger device. Two different type of wax inhibitor are used in this study which are cyclohexane and toluene. As rotation speed is increased, the wax deposit obtained at the cold finger is decreased. However, at the certain minimum point, the amount of wax deposit is increased. For the wax solubility test, temperature was found to be the main effect to the wax. At the highest temperature, the solubility of paraffin wax is increased.

Keywords: wax deposition, waxy crude oil, cold finger device, rotation speed, solubility

ABSTRAK

Deposisi lilin telah menjadi masalah utama dalam bidang minyak dan gas. Ia menjana kejatuhan tekanan tambahan dan menyebabkan pengotoran yang akhirnya meningkatkan kos operasi semasa pengeluaran, pengangkutan dan pengendalian minyak mentah berlilin. Masalahnya dimulakan disebabkan oleh penurunan suhu minyak mentah semasa proses pengangkutan yang akhirnya menyebabkan pemejalan minyak mentah untuk membentuk lilin. The lilin yang memejal biasanya dikeluarkan oleh proses penyaluran. Pemendapan lilin minyak mentah dalam perancangan menjadikan kawasan aliran yang lebih kecil dan lebih kecil dengan masa, yang kemudiannya mempengaruhi kapasiti pengangkutan dan keselamatan operasi talian paip. Terdapat banyak faktor yang mempengaruhi pemendapan lilin: komponen mentah, pengagihan atom karbon parafin, suhu minyak, perbezaan suhu antara minyak dan dinding paip, tempoh pemendapan, kadar aliran, dan sebagainya. Dalam kajian ini kesan kelajuan putaran disiasat terhadap pemendapan lilin. Di samping itu, kesan suhu ke kelarutan lilin juga dikaji. Kerja-kerja eksperimen telah dijalankan dengan menggunakan peranti jari sejuk. Dua jenis yang berbeza lilin inhibitor digunakan dalam kajian ini yang sikloheksana dan toluene. Kelajuan putaran bertambah, deposit lilin yang diperolehi di jari sejuk menurun. Walau bagaimanapun, pada masa minimum yang tertentu, jumlah deposit lilin bertambah. Bagi ujian lilin kelarutan, suhu didapati kesan utama kepada lilin. Pada suhu yang tinggi, kebolehlarutan lilin parafin bertambah.

Kata kunci: pemendapan lilin, minyak mentah berlilin, peranti jari sejuk, kelajuan putaran, kelarutan

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LIST OF ABBREVIATIONS

A	Area
cm	centimetre
r	Radius
rpm	rotation per minute
Q	flow rate
v	linear speed
w	rotation speed

CHAPTER 1

INTRODUCTION

1.1 Introduction

The wax deposition problem has occurred in the oil and gas industry for decade. It gives problem during transportation route because of the shrinking flow area when the deposited waxes become thicker and thicker. It results in the plugging of flow strings, formation damage, loss of hydrocarbons, and increased the production cost (Fadairo Adesina, 2010). An analogy to this is accumulation of cholesterol in the human blood vessel that leads to the obstruction of blood flow through the body from the heart (O.Bidmus, 2010).

1.2 Motivation and statement of problem

The earlier the problem is diagnosed in the life of a reservoir, the easier it will design a preventive or control management plan that will reduce or eliminate some of the technical and economic problem associated with the wax deposition. The technical issue that associated with the wax deposition include :

1) Reduction in the interior diameter of the pipelines and plugging of production and flow channels.
2) Change in the reservoir fluid composition and fluid rheology due to the phase separation as wax solid precipitates.
3) Additional strain on pumping equipment owing to increase pressure drop along the flow channel consequent to rheological changes as wax begins to crystallize.
4) Limiting influence on the operating capacity of the entire production system.

The critical role of economics in the oil production make wax deposition a significant economic concern to the industry due to following :

- Investment and operating cost of the oil and gas industry is expensive so when the blockage due to the wax deposition happen, it used o lot of money to repair the damage.
- It also lead to the lost production.

Flow rate is considered an important factor affecting the wax deposition process. The deposit mass decreases as the flow rate of oil is increased whether it is laminar or turbulent flow.

1.3 Objectives

The following are the objectives of this research:

- To study the effect of rotation speed on the wax deposition using two types of chemical inhibitor.
- To study the solubility of the paraffin wax at different temperature.

1.4 Scope of this research

The following are the scope of this research:

i) Characterization of the Malaysian crude oil for SARA analysis using Test Column Chromatography and wax content.

ii) The effect of rotation speed was run at speed range of 0 rpm to 600 rpm using cyclohexane and toluene as chemical inhibitor on wax deposition.

iii) The solubility of the paraffin wax in toluene at four different temperature at range 30°C to 60°C.

1.5 Main contribution of this work

The following are the contributions:

- Contribution was prior to my supervisor's guidance in determining the correct properties and method to be performed.

1.6 Organisation of this thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 2 provides an overview about wax deposition from crude oil. In this chapter also discuss about mechanism of wax deposition, factors affecting the deposition process. This chapter also provides a brief review on the previous research done about the wax deposition.

Chapter 3 gives a complete description of the experimental apparatus and method applied in the various parts of this study. There are of set of experiments carried out in this study are discussed. The materials used, sample preparation methods, analyses method and experimental procedures and design are described in this chapter.

Chapter 4 covers about result and detail discussion about the experiments are presented.

Finally, Chapter 5 summarizes the important conclusions of this study and some specific recommendations for future work in this area of research are presented.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview of Wax Deposition

Wax deposition is the formation of a layer of the separated solid phase, and the eventual growth of this layer, on the surface in the contact with the crude oils.

Figure 2-1: Wax deposition in pipeline

Wax deposition can be formed from a precipitated solid phase through mechanisms of shear dispersion, gravity settling, Brownian motion and molecular diffusion. The wax deposition have different concept with precipitation. Precipitation does not necessarily lead to deposition. The precipitation is the important condition for deposition but it is not necessarily sufficient for wax deposition.

For the deposition to occur in the pipelines, the following conditions must be fulfilled (Saracoglu, 2000):

1) Pipeline wall temperature must be below the wax appearance temperature (WAT) for the fluid.
2) Negative radial temperature gradient must be present in the flow. That is, the wall temperature must be lower than the centreline temperature. A zero gradient implies that no deposition will occur.

3) Wall friction must be large enough so that wax crystal can stick to the wall.

Some crude oils contain significant amount of wax. The different waxes have in a pure start definite freezing and boiling temperatures. During the production, transportation and storage, the crude oil will attain temperatures lower than freezing temperature of the wax. These temperature is called as wax appearance temperature (WAT). At this temperature, the wax start to form crystals in the fluid and deposits on the vessel walls.

2.1.1 Wax Deposition Mechanisms

There are four mechanisms for wax deposition. There are molecular diffusion, shear dispersion, Brownian diffusion and gravity settling (E.D. Burger, 1981)

2.1.1.1 Molecular Diffusion

Oil flowing at a pipeline is cooled due to the surrounding cold seawater. Molecular diffusion acts as soon as the temperature of the wall reaches the WAT. At that temperature, the oil is saturated with wax in solution and wax precipitates out. Wax precipitation leads to a concentration gradient between dissolved wax in the turbulent core and the wax remaining in the solution in the wall. Due to this, dissolved wax diffuse toward the wall where it is subsequently (Rosvold, 2008)

2.1.1.2 Shear Dispersion

Shear dispersion concerns already formed particles settling on the cold pipe surface due to roughness of the wall and intermolecular forces (Gjermundsen, 2003). When wax crystals are suspended in flowing oil that in laminar motion, the wax crystals tend to move at the mean speed and in direction of the surrounding oil (E.D. Burger, 1981). The shearing of the oil close to the pipeline wall also includes a lateral movement of wax particles known as shear dispersion (Rosvold, 2008). Wax crystals in the oil will migrate towards the wall where they deposit, because of the lower velocity near the wall compared to the centre of the pipe, At the wall the wax may form a deposit on its own or link with wax which is already deposited by molecular diffusion (Bern, 1981).

Parameters likely to affect the shear dispersion mechanism are: (Rosvold, 2008)

- The wall shear rate
- The amount of wax out of solution
- The shape and size of the wax particles

2.1.1.3 Brownian diffusion

Small and solid waxy crystals are suspended in the flowing oil will be bombarded continually by thermal agitated oil molecules. These collisions lead to small random Brownian movement of the suspended wax crystals (E.D. Burger, 1981). At a concentration gradient of these wax crystals, Brownian motion will lead to a net transport which is similar to diffusion (Rosvold, 2008).

2.1.2 Wax Precipitation

Crude oil containing various fractions of heavy n-alkanes precipitate as wax deposits due to either evaporation of volatile light components or a drop in the temperature of the system. Wax precipitation occurs during the formation of solid wax crystals out of solution from a liquid phase, while wax deposition occurs during the formation and growth of layer of precipitated solid on a surface. Wax precipitation can occurs without wax deposition but wax deposition cannot occur without wax precipitation.

2.1.3 Wax Appearance Temperature (WAT

This is an important parameter in wax precipitation and deposition. It is the temperature where the first crystals of wax start to precipitate out the solution while being cooled. It is an essential property in determining the propensity of the crude oil towards wax deposition. Crude oil system with low WAT will be less prone to the precipitate out and deposit wax. As long as the crude oil temperature is above the WAT, there are no wax deposition occurs. Once the temperature drops below the WAT, the wax molecules will begin to precipitate or crystallize out of the solution and wax deposition can occurs. A near-infrared (NIR) scattering technique is used to measure the wax appearance temperature of several petroleum fluids under non-quiescent conditions (K.Paso, 2009)

2.1.4 Wax disappearance Temperature (WDT)

The wax disappearance temperature (WDT) is the temperature at which the wax crystals in a “waxy” mixture become completely dissolved in solution when the mixture is heated from a temperature below its WAT. There is an important distinction between the liquids temperature and the experimentally determined WAT. The liquids temperature defines the true solid-liquid phase boundary, whereas the experimental WAT represents the temperature at which the first crystal are detected upon cooling and this, depending on the sensitivity of the measurement method and the cooling rate, can be subjective. Due to super cooling involved in the crystallization process, the experimental WAT would be lower than the liquids temperature (O.Bidmus, 2010).

2.1.5 Factor that Affecting the Wax Deposition

Wax deposition starts to take place as soon as the pipe wall has a temperature at or below the wax appearance temperature (WAT). There are list of factors that can be considered to affect the value of the wax appearance temperature. This factors which affecting the wax appearance temperature related to the wax deposition process. Among the many factors that affecting the wax deposition in crude oil, the most considered factors are the crude oil composition, temperature, flow or shear rate and deposition time.

2.1.5.1 Composition

Composition of the crude oil can affect the wax deposition. The lower paraffin wax content in the crude oil making the wax deposition less likely to occur. When all the mixture were exposed to identical operating condition, those with a higher wax composition produced more solid deposits. Possibility of deposition will increase as the wax content of crude oil increases. n-paraffin and iso-paraffin tend to cluster together and precipitate from crude oil as wax solids and iso-paraffin are inclined to delay the formation of wax nuclei and usually unstable solids (M.A., 1999).

Naphthene or cyclo-paraffin are stiff and bulky in nature and they tend to disrupt the wax nucleation process while aromatics are good solvents for paraffin wax. Mixture of oil with heavier waxes formed deposits are strong than the mixture with lighter paraffin that formed unstable deposit because unstable deposit can easily flaked off the deposition surface. Wax deposition also can be reduce with presence of asphaltene because deposited asphaltene could serve as nucleation sites for additional wax deposition. Energy barrier required for formation of critical wax nucleus can be decreased by presence of impurities and other amorphous solid in the oil. Other hand, the presence of water also can reduce the amount of wax deposited.

2.1.5.2 Temperature

Heat is transferred through the pipe wall that creates a temperature gradient during the flow of crude oil above the wax appearance temperature, which in turn initiates the deposition of wax solids. As temperature of crude oil and pipe wall or coolant increase, the amount of wax deposition will decreased. The temperature difference between the oil –deposit interface and the pipe-wall is important parameter for wax deposition (A.K. Mehrota, 2005). Wax deposition can be prevented if the crude oil flowing through a highly conductive pipeline is maintained above a certain temperature. It was shown that this temperature could be relatively high for sub-sea pipelines and that it would be energy intensive and uneconomical to maintain the crude oil temperature at this value. It creates a thermal insulation that limits heat transfer and reduces the rate of further increases in the mass deposit as the thickness of the wax deposit increases.

2.1.5.3 Flow Rate or Shear Rate

The shear rate produced while crude oil is flowing causes shear forces that prevent the complete wax gelling of a pipeline by destroying the intermolecular structure as it forms (B.T. Ellison, 2000). Flow rate is considered an important factor affecting the wax deposition process. The deposit mass decreases as the flow rate of oil is increased whether it is laminar or turbulent flow. A sloughing or shearing off of the deposit that increase is caused by the rate of shear at the wall with increasing flow rate. The process starts to occur when the cohesive and adhesive properties of the paraffin wax molecule and the deposition surface are overcome by the rate of shear.

2.1.5.4 Deposition Time and Aging

Due to the thermal insulation provided by the initially deposited solids, the rate at which wax deposits on a surface decreases. The amount of deposition increase with time, irrespective of the operating conditions, until it reaches an asymptotic value at steady state conditions. As the time increases, the wax content in the deposits also increases. This leads to a gradual hardening of the deposit layer with time that is referred to as aging.

The gel-like deposit undergoes a characteristic change with time whereby it become richer in the heavier paraffin content while the lighter paraffin content or the amount of entrapped oil simultaneously decreases during aging. Aging process depend on the operating conditions and that it was a stronger function of the temperature difference across the deposit than of the compressive force due to the flow rates.

2.2 Crude Oils

Crude oil is simply unprocessed oil found deep beneath the earth’s surface. It can range in colour from clear to black and can be found as a liquid or solid. Overall properties of crude oils are dependent upon their chemical composition and structure. Crude oil is pumped and stored in barrels for future refinement. The refinement process may involve filtering, addition of additives, and specialized separation techniques to create specific crude oils and crude oil products. Generally all crude oils are made up of hydrocarbon compounds (Turner, 2014)

Figure 2-2: Crude Oil

Crude oil also a complex homogeneous mixture of various carbon number hydrocarbons, and it compounds of paraffin, aromatics, naphtehne, asphaltenes and resin. The majority of crude oils contains considerable amounts of wax. The composition of the wax depends on the oil. A wax composition of mainly low molecular weight n-alkanes (C_{20}-C_{40}) is termed as paraffin or distillate was (Rosvold, 2008). The wax crystallizes as large needles and plates. A wax composition of high molecular weight iso-alkanes and cyclic alkanes is termed as microcrystalline or amorphous wax.

The largest source of the wax is paraffin wax. The main component of paraffin waxes is n-alkanes and these are considered a natural starting point for understanding the physical and thermal properties of the wax. Paraffin form a crystalline structure below their melting point or melting range from either their individual compound or mixtures with one another.

2.2.1 Physical and Chemical Properties

Crude oil is not a uniform substance since its physical and chemical properties vary from oilfield to oilfield and can even vary within wells at the same oilfield. At one extreme, it is a light, mobile, straw- coloured liquid. At the other extreme, it is a highly viscous, semi-solid, black substance. The lower molecular weight components of petroleum possess moderate to high water solubility while higher molecular weight fractions tend to form emulsions in water. The lower molecular weight components of petroleum have high vapour pressure while higher molecular weight fractions tend to possess negligible to low vapour pressure. The lighter weight aliphatic and aromatic components of petroleum will have high mobility in soils while the heavier molecular weight constituents will possess low mobility. Volatilization is expected to be moderate to high for most constituents of petroleum. The rate of hydrolysis is negligible since paraffin, naphthenes and the aromatic hydrocarbons contained in petroleum do not possess functional groups that hydrolyse under environmental conditions. The rate of atmospheric photo oxidation is expected to be slow to rapid for most components of petroleum.

2.3 Paraffin Wax

Crude oil is the largest single source of paraffin wax. These wax can be classified as macro-crystalline/paraffin wax and micro crystalline wax (Srivastava, 1993). Paraffin waxes are a mixture of normal alkanes of varying chain length (C_{18}-C_{65}) that tend to cluster together and precipitate from crude oil, under the right condition to form wax solids (O.Bidmus, 2010).

Figure 2-3: Paraffin wax

The main component of paraffin waxes are n-alkanes and these are considered a natural starting point to understand the physical and thermal properties of the wax. The n-alkanes are linear chain of hydrocarbons belonging to a family of compounds, the paraffin series, in which all members contain carbon and hydrogen in proportions given by the formula C_nH_{2n+2} (Turner W. , 1971).

2.3.1 Physical and Thermal Properties

Paraffin belong to a homologous series where each successive member of the series differs constantly from the next CH_2 group (O.Bidmus, 2010). Pure waxes are colourless, odourless, and tasteless solids. The yellow colour that precipitates out of solution to foul pipelines is usually due to other impurities and other deposits. High molecular weight paraffin waxes can be hard and brittle, whereas lower molecular weight paraffin waxes are generally and malleable (Becker, 1997). They are not as dense as water and do not dissolve easily in water.

The physical state of paraffin wax is highly dependent upon factor such as temperature and pressure, where multiple physical state of wax can coexist under specific. Its physical properties are also determined by the length the longest, uninterrupted, linear alkane constituent. Paraffin waxes are solid at room temperature and typically start melting between 50°C and 70°C (Schmidt, 2010). However, much greater melting points are observed for waxes with heavier content. Generally, the boiling and meting points of paraffin increase with increased content of longer, heavier alkanes, whereas the boiling point decreases with increased branched alkane content.

An alkane molecule is held together entirely by covalent bonds. These bond are directed in a symmetrical way, so that the slight bond polarities tend to cancel out resulting in either a non-polar or very weakly polar molecule. Weak and short-range van der Waals forces that act only between the surfaces of the molecules hold the non-polar molecules together. So, it is observed that the larger the n-alkanes molecule, the stronger the intermolecular forces (O.Bidmus, 2010).

The intermolecular forces between paraffin molecules are London Dispersion forces (Van der Waal force). Bigger molecules exhibit greater Van der Waal forces, which increase the boiling point of the molecules. Branching decreases the magnitude of Van der Waal forces by preventing the attainment of optimal proximity of the molecules to each other, and lowers the boiling point. Because the melting point of paraffin mostly depend on how well the molecules fit into a crystal lattice, less regularity in the trend is observed as seen in Figure 0-4.

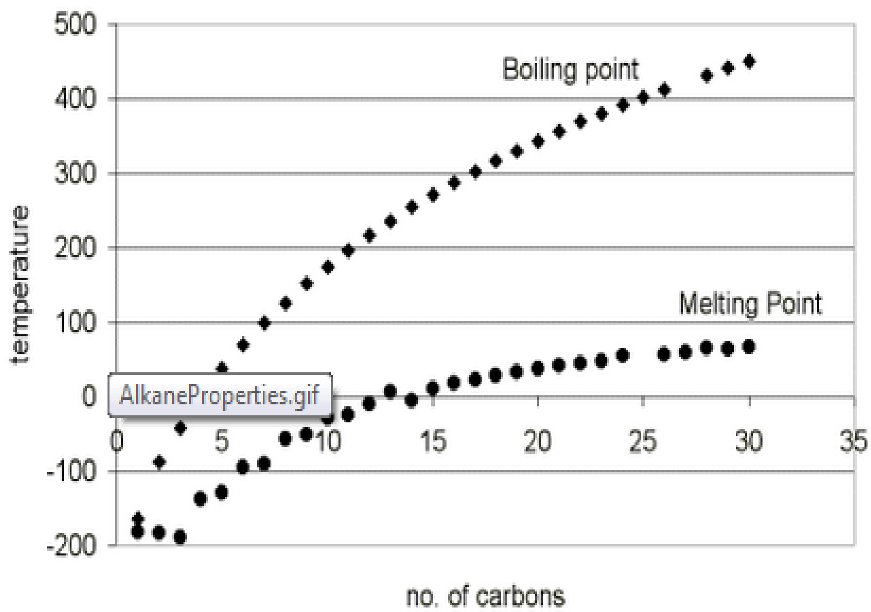

Figure 2-4: Melting Points and Boiling Points of unbranched hydrocarbons, temperature in °C

2.3.2 Structure

Paraffin hydrocarbons forms a crystalline structure below their melting point or melting range from either their individual compound or mixtures with one another

(O.Bidmus, 2010). Typical paraffin waxes in crude oil have a clearly defined crystal structures composed of macroscopic crystals. The crystal form of paraffin wax is called the macro-crystalline (individual crystals visible to the unaided eye C_{18} to C_{30}). Macro-crystalline paraffin are usually hexagonal or needle shaped (orthorhombic).Under the most favourable conditions, n-paraffin form clearly defined orthorhomic crystals (the orthorhombic crystal structure is one of the seven lattice point groups), but unfavourable conditions and presence of impurities lead to hexagonal and/or amorphous crystallisation (Becker, 1997).

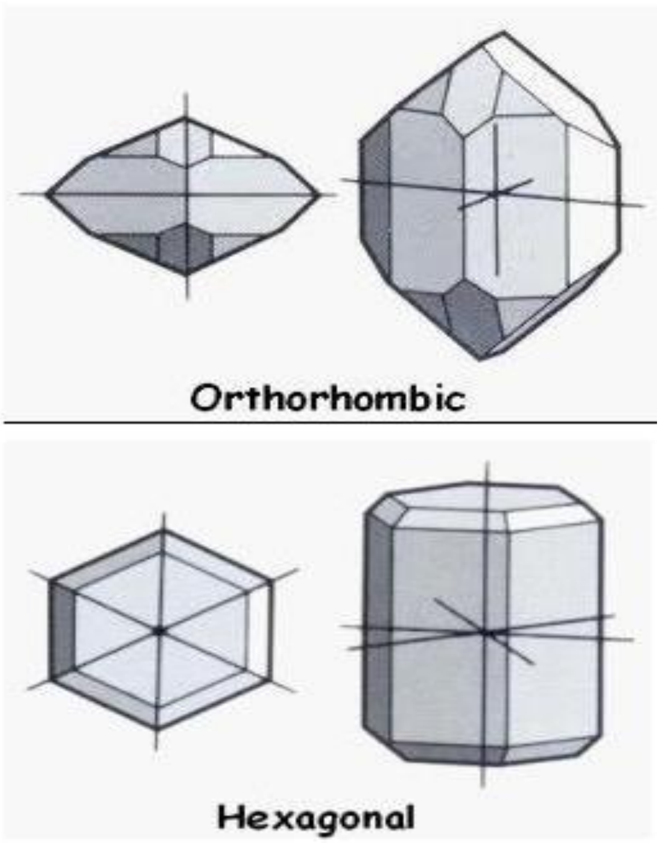

Figure 2-5: Hexagonal Crystal Structure and Orthorhombic Crystal Structure

2.3.3 Solubility

Paraffin waxes are non-polar, therefore, they are insoluble in water but are soluble in other non-polar petroleum based solvents of similar structure. The solubility of paraffin wax in petroleum oils at various temperatures, and of the effect of viscosity of solvent and the melting point of the wax upon solubility, is of considerable practical value in filter-pressing wax distillates to remove the wax. It is also useful in making calculation s involving the refrigeration of wax-bearing oils. Solubility data in the literature consist principally of figures for supposedly pure hydrocarbons from either synthetic or natural sources, in the usual organic solvents.

2.3.3.1 Effects of temperature on solubility

For the effects of temperature on solubility, there are two cases:

1) As the temperature of a liquid increases, the solubility of the gases in that liquid decrease.
2) As the temperature of a liquid increases, the solubility of solid in that liquid increases.

Paraffin wax deposits are solid at standard conditions. The addition of more heat to wax containing crude will facilitate the dissolving reaction by providing energy to break bonds in the solid. Therefore, adding heat to the oil makes it easier for the particle to move around between the solution and the solid, and causes the wax to melt by providing the necessary energy to break the bonds in the solid and enter into solution. The Second Law of Thermodynamics also predicts that entropy always increase in a spontaneous process, in that particles favours disorder. Therefore, equilibrium will favour a solution state with increase temperature.

2.3.3.2 Effects of melting point on solubility

When a molecular substance dissolves in water, the intermolecular forces within the substance need to be broken. The higher the melting point, the stronger the intermolecular forces and the more stable the crystal lattice structure (Becker 1997). Paraffin waxes with a higher melting point will need more energy to dissolve in water than paraffin waxes with a lower melting point. Therefore, solubility decreases as melting point of paraffin wax crude increases.

2.3.3.3 Effect of viscosity on solubility

Viscosity refers to a fluid's resistance to flow. Increased polymerization (addition of CH_2) increases the molar weight of the fluid. The heavier the fluid, the more resistance it will have to flow. An increase in the length of carbon chains also leads to an increase in intermolecular attractive forces, as well as an increase in the extent to which nearby molecules become entangled when they have an extended shape. This means that the boiling point and melting point of the fluid increase as more energy is needed to overcome the intermolecular forces. Thus, solubility decreases as viscosity increases.

2.3.3.4 Effects of pressure on solubility

Liquids and solids show very little change in solubility with changes in pressure, if any. Pressure is not as influential on paraffin as temperature, but does impact its solubility due to the change in composition. Light hydrocarbons (C_{16-}) act as solvents in crude and will come out of the solution when pressure drops. This decreases the concentration of the solvent. As a result, waxy molecules (C_{16+}) precipitate sooner than they would if the pressure had not dropped.

2.3.4 Stability and Reactivity

Paraffin wax stable and non-reactive under ordinary conditions of use and storage and is unaffected by most common chemical reagents; however, it does burn readily if ignited. Paraffin will also react with halogens under UV, light or heat. When heated at high temperatures in the absence of air, paraffin wax can also crack and break up into smaller, lighter paraffin molecules.

2.3.5 Flow Properties of Waxy Crude Oils

The most common crude oil in the petroleum industry is waxy crude. From an environmental viewpoint, waxy crude are very important since they have low sulfur content. Additionally, their accessibility joined with the requirement for new wellsprings of petroleum has empowered creation of these unrefined oils. Nonetheless, wax agglomerates expand the obvious thickness of this oil which builds the vitality necessities connected with pipeline transportation. Since the temperature at which paraffin solidifies is not especially low (as a rule between 10° C and 30° C), the issue of crystallization influences the majority of the waxy rough oils that are found in natural.

Oil producers have been aware of the difficulties of pipelining waxy crude oil and fuel oils for several decades. Traditionally the issue has been avoided by heating the crude or the crude and the pipeline, thus holding the wax in solution (El-Eman N., 1993). Flow of waxy crude can be improve by many of ways. From (Marsden S., 1988), the viscosity to nearly that of the continuous water phase can be reduce by an oil in water (O/W) emulsion. Blending with a less waxy crude oil also improves the flow properties by altering the wax solubility relationships (Marsden S., 1988). More recently, chemical additives, for example pour point depressants, flow improvers, paraffin inhibitors, or wax crystal modifiers have been developed. Small quantities of